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Rate of the O + SO_3 reaction

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The rate of the O + SO_3 reaction has been measured under pseudo-first-order conditions in a discharge flow reactor with ESR detection. The reaction is shown to be a fast third-order process at pressures up to 7 torr, a fact not brought out in previous work. Third-order rate constants obtained for M = He at 298, 385, and 507°K are 7.3 ± 0.2, 3.8 ± 0.2, and $2.4\pm0.2\times10^{17}$ cm^6 mole^{-2}·sec^{-1}, respectively, the data obeying $k = 5.0\times10^{16}\exp(785/T)$ in this range. At 298°K, the ratio $k(M = N_2)/k(M = He)$ is 1.4, and it is shown that the ratio $k(M = SO_3)/k(M = He)$ probably cannot be greater than about 10. The reaction products are written as $SO_2 + O_2$, no evidence being found for a stable SO_4 in the gas phase. Analogous measurements on N + SO_3 indicate it is too slow to measure by this technique (bimolecular rate constant $<6\times10^6$ cm^3 mole^{-1}·sec^{-1}), in disagreement with other reported results.

INTRODUCTION

The reaction of O atoms with SO_3 has received very little kinetic attention, the situation having been covered in a recent review.[1] Written in the bimolecular form $O+SO_3\rightarrow SO_2+O_2$, the gas phase reaction is usually quoted as being very slow at room temperature, an opinion based entirely on the early work of Kaufman,[2] who attributed the decay of O (monitored by the NO afterglow) in a fast flow experiment upon adding SO_3 to an increased wall recombination loss. Much more recently, Jacob an and Winkler[3] reported a gas phase bimolecular rate constant of 3×10^7 cm^3 mole^{-1} · sec^{-1} at 300 °K from a discharge flow experiment with low temperature trapping of products, a value also indicating a very slow reaction. These authors noted SO_4 as being a probable intermediate. Aside from rather ill-defined results from flame experiments,[4] no other data on the $O+SO_3$ system are available.

In the present paper, we report a new study of this reaction which clearly demonstrates that it is a fast third-order process in the 0–7 torr regime, and presents some information on its temperature dependence. Some remarks on the $N+SO_3$ reaction are also offered.

EXPERIMENTAL

The fast flow system with ESR detection used in this work has been described in detail previously.[5] O decays under pseudo-first-order conditions were monitored with the ESR cavity at a fixed position and excess SO_3 flows metered into the movable injector, the O being furnished by a microwave discharge in a trace of O_2 carried in helium. The apparatus was altered from previous descriptions to the extent that a quadrupole mass spectrometer (Extranuclear Laboratories) was used for continuous online analysis of stable species, sampling being accomplished by way of a Pyrex probe located at a fixed position 16 cm downstream of the center of the ESR cavity. The probe orifice was 0.25 mm in diameter, and normally the entire flow from this probe was fed to the quadrupole mass filter inlet, although a bypass pumpoff line was provided in the system between the orifice and the quadrupole inlet. At a reactor pressure of 2 torr helium the pressure downstream of the sampling orifice was about 20μ, so that effective quenching was accomplished.

The main experimental problem in this work was that of controlling and metering the substantial flows of SO_3 required. Liquid SO_3 in its "stabilized" form ("Sulfan" from Allied Chemical Corp. containing 0.2% dimethyl sulfate) was kept in a glass reservoir at room temperature, where its vapor pressure is about 400 torr. Some samples were not entirely successfully stabilized in the liquid state, and occasional mild warming was necessary to melt the crystals which formed. The reservoir was isolated when not in use by a stopcock lubricated with fluorosilicone grease, as were other stopcocks in the SO_3 flow lines. This grease was very gradually attacked and blackened, but not so drastically as to be unusable. The SO_3 was throttled from its vapor pressure by means of a stainless steel needle valve, and then led to the reactor through Teflon tubing. After a few minutes at a given needle valve setting, the flow rate of SO_3 steadied down to a satisfactorily constant level.

According to our usual procedure when using corrosive and difficult gases, measurement of the SO_3 flow rate was carried out for each fixed needle valve setting after a given kinetic run had been completed by switching the flow from the movable injector to a calibrated volume and timing the pressure rise. The flow measurement was repeated several times until satisfactory reproducibility was evident (~ 5%), the usual experience being that the first calibration run of the day tended to be low owing to serious SO_3 adsorption and/or condensation in the calibration volume. After a couple of exposures to the SO_3 vapor, the system became saturated and reproducible calibrations could be attained. The manometer fluid used in the calibration system was Kel-F oil, which also was gradually attacked and had to be occasionally renewed. The oil density was not affected after prolonged exposure to SO_3, a point of concern which was checked by comparing the oil manometer readings against a mercury manometer using argon pressures. The oil manometer was also checked against a quartz spiral manometer using SO_3 itself to prove that SO_3 was not being absorbed appreciably by the oil. SO_3 flow rates in the range 0.05–1 cm^3·atm sec^{-1} were successfully provided in this way.

Most of the experiments were carried out using helium carrier gas. This was even more desirable in the present case than usual because of the greater difficulty in achieving rapid mixing of the high molecular weight SO_3 added through the movable injector, particularly at the higher reactor pressures. Experiments using injected NO for qualitative visual observation of mixing by means of the O+NO chemiluminescence clearly showed that in N_2 carrier at 1 torr reactor pressure and linear velocity about 1600 cm/sec mixing was essentially complete at a distance of 3–4 cm from the tip of the six-hole injector, while at 5 torr with the same N_2 flow (and therefore lower linear velocity) the mixing region was seen to extend 20–30 cm downstream. Similar experiments in helium carrier, however, showed the mixing region at 5 torr shortened to about 5 cm, undoubtedly owing to the higher diffusion coefficient of the injected NO in He than in N_2. The poor mixing in N_2 also showed up as initial curvature of the logarithmic O decay plots at pressures above about 3 torr. Thus, precise measurements were confined to helium carrier, the closest point of measurement being taken with the probe tip 18 cm from the ESR cavity center. The use of discharged N_2 carrier was also complicated by a greater instability in the ESR readings even under good mixing conditions. This may have been due to small amounts of residual N (or NO) from the N+NO titration used to furnish the O atoms, and the formation of N–O–S complexes of some kind. Nevertheless, a few runs in N_2 carrier at pressures below 2 torr were carried out with some success.

The reactor was used with "clean" walls, i.e., no coating was deliberately applied, but the fact of injecting substantial quantities of easily condensible SO_3 (with several complex allotropic condensed forms)[6] plus a possible condensible SO_4 product leaves no illusions that the reactor walls stayed clean very long. Occasionally the reactor was baked out or removed and cleaned with dilute HNO_3, acetone, and water. Nevertheless, no long term losses in O signal were observed over periods of a few weeks which would have been attributable to "dirtying" of the reactor walls. One rather striking type of behavior was noted which deserves comment, however. In early experiments, the tank gases He and O_2 (stated purity better than 99.99%) passed through the discharge were used without further treatment, as has been our usual practice. The addition of SO_3 then caused a gradual deterioration of the ESR cavity Q value (not observed unless the discharge was on) and a resultant decrease in O signal under otherwise fixed conditions during the course of a day's running. Guessing that this might be due to traces of H_2O being dissociated in the discharge and possibly forming some highly polar substance (H_2SO_4?) which gradually coated the flow tube in the cavity region, a liquid N_2 trap was inserted in the flow line just upstream of the discharge. This procedure eliminated the gradual Q deterioration entirely, and the O signals were quite reproducible over several hours running, so it is likely that a trace of moisture in the inlet gases was correctly diagnosed as the cause of the problem. Since then an independent report of difficulties with residual moisture in tank gases has appeared[7] in another context.

Experiments were performed at room temperature and at 385 and 507 °K. Higher temperatures were precluded by the fact that SO_3 begins to undergo appreciable decomposition, while below room temperature there would be problems of condensation in the injector probe.

To our knowledge there have been no reported quantitative studies of the mass spectrometry of SO_3, which is not surprising in view of its unpleasant properties. Its tendency to adsorb strongly makes background corrections very difficult, and steady mass readings are attained only rather slowly, a problem also noted earlier by others.[8] It was thus completely impractical to carry out measurements of pseudo-first-order SO_3 decay in the presence of excess O, which would have been a desirable complementary procedure to the reverse approach followed here. SO_3 was normally monitored at m/e 80 when necessary, which avoided interference from any SO_2 product at m/e 64 and 48. Pronounced decreases in the m/e 80 peak were easily observable when the discharge was turned on (with SO_3 flows such that it was not in large excess over O), thus showing conclusively that a true O+SO_3 reaction was occurring and not simply a catalyzed recombination of O.

RESULTS AND DISCUSSION

The measurements of O decay under pseudo-first-order conditions were very well behaved in general, the O signals responding crisply as the SO_3 was turned on and off, or as the SO_3 injector position was changed. There was no evidence of the long, sluggish recovery period upon turning off the SO_3 which was noted in the

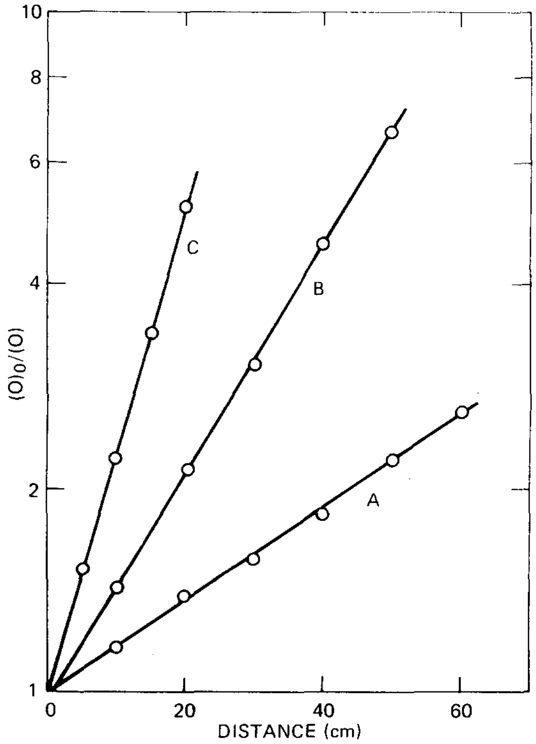

FIG. 1. Examples of O decay plots. T 298 °K, He carrier.
A: $P = 0.75$ torr, $v = 1600$ cm/sec, SO_3 mole fraction = 0.0181.
B: $P = 2.66$ torr, $v = 1670$ cm/sec, SO_3 mole fraction = 0.0046.
C: $P = 4.08$ torr, $v = 1400$ cm/sec, SO_3 mole fraction = 0.0036.

early study[2] using the O + NO chemiluminescent monitoring technique, and the stability and reproducibility of the O signals was not significantly inferior to that observed in less difficult reaction systems. This in itself would suggest that wall losses were probably not a serious complication, but since this was a worrisome point, more specific evidence was required, as presented below. Since there was no effect of injector movement on the O signal at the fixed cavity with the SO_3 flow off, all decays were taken simply with the SO_3 on continuously, no "on-off" procedure being necessary.[5] The logarithmic O decay plots were of good linearity over a considerable range, as Fig. 1 illustrates.

Experiments at different reactor pressures (Table I) quickly revealed that the $O+SO_3$ reaction was not a simple bimolecular case but was pressure dependent, and interpretation in a third-order regime was appropriate. To take account of possible differences in third-body efficiency and wall reactions, one can write

$$O+SO_3+He\xrightarrow{k_1}\text{products}$$

$$O+SO_3+SO_3\xrightarrow{k_2}\text{products}$$

$$O+SO_3+\text{wall}\xrightarrow{k_3}\text{products}$$

$$O+\text{wall}\xrightarrow{k_4}\text{products},$$

where the k_3 step includes any bimolecular homogeneous contribution as well as a wall reaction which depends on the gas phase SO_3 concentration, while the last step is a simple first-order wall loss with a k_4 requiring the presence of some SO_3 (say as an adsorbed layer) but having a value independent of its concentration. k_4 is thus important only in the region of the reactor downstream of the movable SO_3 injector. (Note that any wall loss *independent* of the presence or absence of SO_3 cancels out in the fixed detector–movable injector scheme.)[9] Under pseudo-first-order conditions when $(SO_3) \gg (O)$, with an SO_3 mole fraction x and a total molar concentration $N (= P/RT)$, the O decay equation becomes

$$vS = k_1x(1-x)N^2 + k_2x^2N^2 + k_3xN + k_4, \tag{1}$$

where S is the decay slope $d\,ln[(O)_0/(O)]/dz$, and v is the linear velocity. At a fixed reactor pressure so that N is constant, a plot of vS against x has an intercept equal to k_4, and it is strictly linear only if $k_1 = k_2$. But

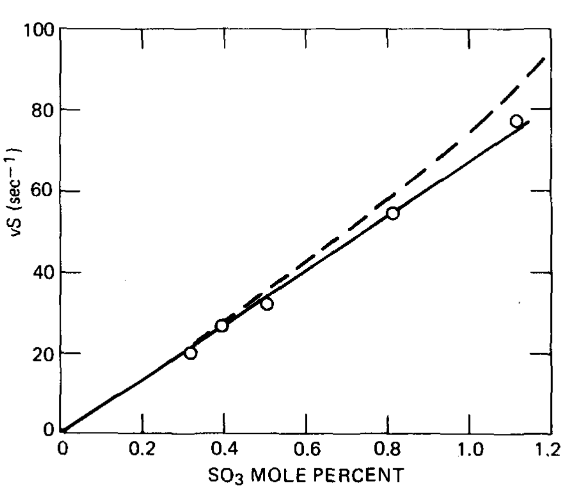

FIG. 2. O decay rates $d\ln[(O)_0/(O)]/dt = vS$ as function of SO_3 mole fraction at constant pressure. $P = 1.77$ torr, $T = 298$ °K, M = He. Dashed line was calculated for $k_2/k_1 = 10$.

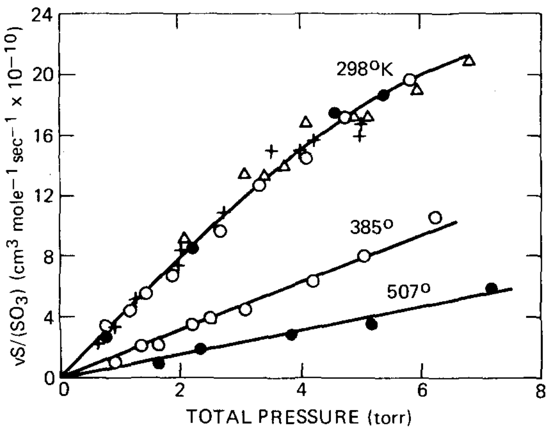

FIG. 3. Dependence of $O+SO_3$ rate constant on total pressure. M = He. Different symbols distinguish runs on different days.

TABLE I. Kinetic data on $O+SO_3+M$. (Typical set only for M = He at 298 °K.)

Helium carrier

T (°K)	P (torr)	Flow rate ($cm^3 \cdot atm\ sec^{-1}$) He	O_2	SO_3	v (cm/sec)	$vS/(SO_3)$ ($cm^3 mole^{-1} \cdot sec^{-1}$)
298	0.75	12.2	0.02	0.22	1600	3.4×10^{10}
	1.18	23.2	0.02	0.21	1910	4.4×10^{10}
	1.45	33.4	0.02	0.21	2240	5.6×10^{10}
	1.87	45.9	0.02	0.21	2380	6.7×10^{10}
	2.66	45.9	0.02	0.21	1670	9.7×10^{10}
	3.34	45.9	0.02	0.21	1340	12.9×10^{10}
	4.08	58.9	0.04	0.21	1400	14.5×10^{10}
	4.73	64.5	0.04	0.22	1330	17.2×10^{10}
	5.80	75.4	0.04	0.11	1260	19.7×10^{10}
385	0.91	10.4	0.08	0.44	1500	1.0×10^{10}
	1.35	26.6	0.08	0.31	2500	2.1×10^{10}
	1.62	26.6	0.08	0.31	2080	2.2×10^{10}
	2.20	46.2	0.08	0.31	2640	3.5×10^{10}
	2.50	46.2	0.08	0.31	2330	3.9×10^{10}
	3.10	46.2	0.08	0.31	1880	4.5×10^{10}
	4.19	59.4	0.08	0.31	1790	6.3×10^{10}
	5.06	69.4	0.08	0.31	1730	8.1×10^{10}
	6.23	69.4	0.08	0.18	1400	10.6×10^{10}
507	1.64	24.3	0.08	0.28	2440	0.9×10^{10}
	2.35	24.3	0.08	0.28	1730	1.8×10^{10}
	3.84	41.2	0.08	0.28	1790	2.8×10^{10}
	5.19	41.2	0.08	0.14	1320	3.6×10^{10}
	7.18	54.4	0.08	0.14	1250	5.9×10^{10}

Nitrogen carrier

T (°K)	P (torr)	Flow rate ($cm^3 \cdot atm\ sec^{-1}$) N_2	NO	SO_3	v (cm/sec)	$vS/(SO_3)$ ($cm^3 mole^{-1} \cdot sec^{-1}$)
298	0.48	3.3	⋯	0.20	720	2.1×10^{10}
	0.69	8.7	⋯	0.20	1260	3.8×10^{10}
	0.75	13.1	⋯	0.31	1740	4.6×10^{10}
	0.84	13.7	⋯	0.21	1620	5.2×10^{10}
	1.10	19.1	0.02	0.26	1710	6.4×10^{10}
	1.10	21.5	0.02	0.28	1900	6.2×10^{10}
	1.27	22.8	⋯	0.32	1760	6.8×10^{10}
	1.35	27.8	⋯	0.15	2010	8.1×10^{10}
	1.65	21.3	0.03	0.16	1270	10.0×10^{10}
	1.72	36.3	0.02	0.26	2070	8.8×10^{10}
	1.85	30.7	⋯	0.10	1620	10.2×10^{10}
	1.87	22.8	⋯	0.33	1190	9.4×10^{10}

if *both* the conditions $x \ll 1$ and $k_2x/k_1 \ll 1$ are fulfilled, the plot will be essentially linear. The results of a series of experiments at constant pressure and varying SO_3 mole fraction are shown in Fig. 2. The reaction is fast enough that under our attainable conditions only a rather limited x range could be covered. Since the data are clearly in the range $x \ll 1$, the linearity of the plot suggests that k_2/k_1 cannot be greater than roughly 10. The dashed line in Fig. 2 was calculated for $k_2/k_1 = 10$, and such a deviation from linearity should have been detectable experimentally. The zero intercept shows that the first-order wall loss k_4 is negligible. The linear slope through the points in Fig. 2 yields a third-order rate constant (M = He) of 7.6×10^{17} $cm^6 mole^{-2}\cdot sec^{-1}$.

In view of the above results, we can rewrite Eq. (1) for the case where $k_4 = 0$, $x \ll 1$, $k_2x/k_1 \ll 1$, in the form

$$vS/xN = k_1N + k_3 . \tag{2}$$

The data on $vS/xN = vS/(SO_3)$ at three different temperatures are plotted against total reactor pressure (i.e., N) in Fig. 3. The reasonable extrapolations through zero intercept make it clear that the other wall loss term k_3 is also negligible.

The room temperature data are linear with pressure up to about 4 torr and then show signs of curvature, while the data at the other two temperatures are linear throughout the range covered. From the linear slopes in Fig. 3, the third-order rate constants (M = He) obtained are 7.3 ± 0.2, 3.8 ± 0.2, and $2.4\pm0.2\times10^{17}$ $cm^6 mole^{-2}\cdot sec^{-1}$ at 298, 385, and 507 °K, respectively, the error limits shown being derived from the probable errors in the least squares slope. The result at 298°K is in excellent agreement with the 7.6×10^{17} derived from Fig. 2 at a constant pressure of 1.77 torr. Twelve runs with $M = N_2$ given in Table I (not shown in Fig. 3) at 298 °K over the range 0.5–1.9 torr also gave a good linear plot through the origin, the slope of which yielded a third-order rate constant of 10×10^{17}. This is 40% higher than the M = He value, which is reasonable enough. The He data are plotted in Arrhenius form in Fig. 4, showing the "negative activation energy" typical of reactions in the third-order regime. The data obey $k = 5.0\times10^{16}\exp(785/T)$ $cm^6 mole^{-2}\cdot sec^{-1}$ over the temperature range covered.

Whether the curvature above about 4 torr in the room temperature plot of the apparent bimolecular rate constant against pressure in Fig. 3 is a real onset of transition to the second-order regime or is an experimental artifact of some kind is difficult to establish. A similar effect was noted[10] in the $OH+NO_2$ and $OH+NO$ reactions at the lowest temperature (273 °K) studied. The pressure seems quite low for an observable deviation from third-order kinetics, although very few reliable studies on radical-molecule reactions of this type over a wide pressure range have been reported. Morley and Smith[11] found the $OH+NO_2$ reaction to be in its transition region over the whole range of measurement 20–300 torr at both 300 and 416 °K, while Anderson and Kaufman[12] observed an apparent onset of transition in the 4–10 torr range for the same reaction at room temperature, although this was later[13] attributed to deviation from strictly one-dimensional flow as discussed below. Thus, it is conceivable that the similar behavior in the $O+SO_3$ case is a real effect. The transition region would be expected to shift to higher pressures with increasing temperature, as the data seem to indicate.

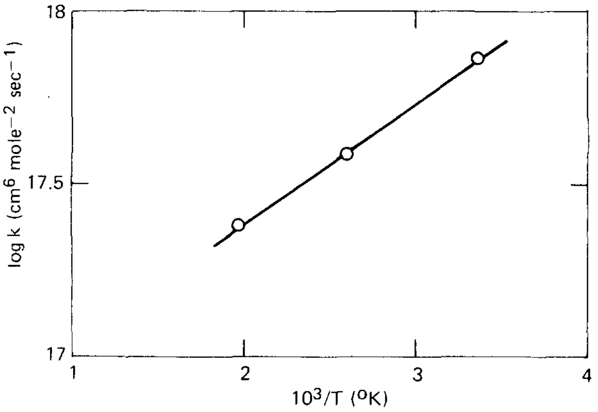

FIG. 4. Arrhenius plot of rate constant for $O+SO_3+He$.

It is difficult to think of purely experimental effects which would give such a curvature with pressure. The effects of radial diffusion in the reactor, i.e., a deviation from simple one-dimensional "plug flow" as assumed in the data analysis, come first to mind. This problem has been treated most recently by Poirier and Carr.[14] For the case where wall losses are negligible, as in the present work, their analysis indicates that the deviation in the measured O decay slope from the one-dimensional limit would be negligible for any value of the parameter $\alpha = D/kr^2$ greater than about 0.3, D being the atom diffusion coefficient, k the first-order gas phase rate constant (i.e., vS), and r the reactor radius. Since this parameter tends to decrease as the pressure increases, the direction is qualitatively correct to cause progressively greater negative deviations in the measured slopes as observed. But under all conditions used in these experiments, α was always greater than 0.5, and it seems unlikely that nonunidimensionality could cause the curvature. Thus, it may be different from the $OH+NO_2$ case where wall losses are appreciable and radial gradients more pronounced.

There seems to be no way of reconciling the present data with those of Jacob and Winkler.[3] Their results were obtained with $M = N_2$ at a total pressure of 2 torr, for which they found a bimolecular rate constant of 3×10^7 at 300 °K. Experiments at 413 and 500 °K indicated a positive activation energy of about 1 kcal/mole. Since our result for $M = N_2$ at 298 °K at a pressure of 2 torr gives a bimolecular rate constant of about 11×10^{10}, the discrepancy is very large. The temperature dependence noted in the present work is also opposite to that of Jacob and Winkler.

The simple Lindemann-type mechanism which would be written for this reaction is

$$O+SO_3 \underset{k_d}{\overset{k_f}{\rightleftarrows}} SO_4^*$$

$$SO_4^* + M \xrightarrow{k_s} SO_4 + M .$$

Whether a stabilized SO_4 could exist in the gas phase as a major reaction product seems quite problematical. We could find no evidence at all in the mass spectrometer for a product at m/e 96, although it was diligently sought, but it should be emphasized that decomposition of SO_4 could have occurred during the sampling process itself. That SO_2 was a product—at least after the sample reached the mass spectrometer—was indicated by the fact that the m/e 64 and 48 peaks did not show as large a fractional decrease upon turning on the 0 discharge as the m/e 80 peak (under conditions where SO_3 was not in large excess). Jacob and Winkler[3] reported a "white metastable solid that condenses at -10°C (thought to be SO_4)" as a product of the reaction, which sublimed to SO_2 and O_2. Actually, there is no reliable evidence for the existence of SO_4 in the gas phase with even a moderate lifetime, although it has been postulated[15] in polluted atmospheres. The evidence for its existence as a solid rests on the work of Wannagat and Rademachers,[16] who reported that discharged SO_2–O_2 or SO_3–O_2 mixtures gave a solid polymer of empirical formula somewhere between S_2O_7 and SO_4 condensible at 0–20 °C, but the role of gas phase reactions in this process is certainly not clear. It is interesting that Wannagat and Schwarz[17] were unable to repeat the original reported SO_4 preparation of Schwarz and Achenbach,[18] and were of the opinion that monomeric SO_4 could not exist on theoretical grounds.

In view of the above uncertainties and the mass spectrometer detection of SO_2 as a product in these experiments, it seems preferable to write the "stabilization" reaction as $SO_4^* + M \rightarrow SO_2 + O_2 + M$. The O_2 product in its triplet ground state also lends some comfort in correlating with the $O(^3P)$ reactant, although the rigor of the spin conservation rules in third-order reaction regimes may not be infallible. A step involving an $SO_4^* + M$ collision is clearly necessary to account for the pressure-dependent bimolecular rate constant observed, but whether this really results directly in the products $SO_2 + O_2$ or in the more conventional vibrational relaxation of SO_4^* has not been definitely decided here—a point worth noting once more. The former route seems perfectly feasible, and perhaps both operate simultaneously in view of Jacob and Winkler's finding of some condensible metastable product from the reaction.

Written as $O + SO_3 + M \rightarrow SO_2 + O_2 + M$, the over-all exothermicity of the reaction is 36 kcal/mole, which may seem rather low for such a fast termolecular process ($k_1 = 7.3 \times 10^{17}$ at 298 °K for M = He). This may be compared with the similarly fast reactions $OH + NO \xrightarrow{M} HNO_2$, $OH + NO_2 \xrightarrow{M} HNO_3$, and $O + SO \xrightarrow{M} SO_2$, all of which have termolecular rate constants in the 10^{17} range with inert gas third bodies and have exothermicities of 49, 49, and 132 kcal/mole, respectively. Simple recombination—dissociation theory would correlate an increasing rate with increasing exothermicity (for reactions of similar "complexity"), but such energy correlations must be viewed with considerable skepticism. A case in point is $O + SO_2 \xrightarrow{M} SO_3$, which has a rather low rate constant in the 10^{14}–10^{15} range (still rather uncertain) but a large exothermicity of 83 kcal/mole.

APPENDIX: THE N + SO_3 REACTION

A study of the reaction $N + SO_3 \rightarrow SO_2 + NO$ (68 kcal/mole exothermic) by both the low temperature trapping technique and by titrating residual N with NO at a series of reaction times was included in the paper by Jacob and Winkler.[3] Results from both methods gave a value for the bimolecular rate constant at 300 °K of about 3×10^8 $cm^3\, mole^{-1} \cdot sec^{-1}$. Thus, their value for this spin-forbidden reaction was an order of magnitude higher than their value for $O + SO_3$.

We have made several attempts to measure a rate for $N + SO_3$, but have found it immeasurably slow by our flow technique. The method was exactly analogous to that used for $O + SO_3$, except that a few percent of N_2 (instead of O_2) was added to the He carrier flowing through the discharge to furnish a trace of N for ESR detection, and then a great excess of SO_3 was metered through the movable injector. Use of the He carrier was desirable both for mixing reasons as discussed earlier, and to avoid the copious quantities of vibrationally excited N_2 present in discharged N_2 at several torr pressure. A typical experiment had the following flow rates (in $cm^3 \cdot atm\, sec^{-1}$): He = 4.0, N_2 = 0.12, SO_3 = 0.55. At a reactor pressure of 3.1 torr, the linear velocity in our flow tube was then 145 cm/sec at room temperature. Thus, for a reactor length of 60 cm, the total reaction time available was about 400 ms, which is comparable to those used by Jacob and Winkler. Under these conditions a rate constant as large as 3×10^8 would have caused the N concentration to drop by a factor 10 over the reactor length, but we observed no detectable change in N at all. Assuming an error in measuring the decay of 5%, i.e., the N could have dropped by 5% over 60 cm, this would put an upper limit on $k(N + SO_3)$ of about 6×10^6 $cm^3\, mole^{-1} \cdot sec^{-1}$. Thus the reaction appears to be very slow indeed, as might be expected from its violation of spin conservation.

[1] K. Schofield, J. Phys. Chem. Ref. Data 2, 25 (1973).

[2] F. Kaufman, Proc. R. Soc. A 247, 123 (1958).

[3] A. Jacob and C. A. Winkler, Chem. Soc. Faraday Trans. I 68, 2077 (1972).

[4] E. L. Merryman and A. Levy, *Thirteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, Pa., 1971), p. 427.

[5] A. A. Westenberg and N. deHaas, J. Chem. Phys. 50, 707 (1969), and earlier references noted therein.

[6] R. C. Brasted, *Comprehensive Inorganic Chemistry* (Van Nostrand, Princeton NJ, 1961), Vol. VIII, p. 134.

[7] I. R. Slagle, J. A. Samlaska, F. J. Pruss, and D. Gutman, J. Phys. Chem. 78, 208 (1974).

[8] A. Levy and E. L. Merryman, Combust. Flame 9, 229 (1965).

[9] A. A. Westenberg and N. deHaas, J. Chem. Phys. 46, 490 (1967).

[10] A. A. Westenberg and N. deHaas, J. Chem. Phys. 57, 5375 (1972).

[11] C. Morley and I. W. M. Smith, Chem. Soc. Faraday Trans. II 68, 1016 (1972).

[12] J. G. Anderson and F. Kaufman, Chem. Phys. Lett. 16, 375 (1972).

[13] J. G. Anderson, J. J. Margitan, and F. Kaufman, J. Chem. Phys. **60**, 3310 (1974).

[14] R. V. Poirier and R. W. Carr, J. Phys. Chem. **75**, 1593 (1971).

[15] P. A. Leighton, *Photochemistry of Air Pollution* (Academic, New York, 1961), p. 236.

[16] U. Wannagat and J. Rademachers, Z. Anorg. Allg. Chem. **286**, 81 (1956).

[17] U. Wannagat and R. Schwarz, Z. Anorg. Allg. Chem. **286**, 180 (1956).

[18] R. Schwarz and H. A. Achenback, Z. Anorg. Allg. Chem. **219**, 271 (1934).